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PERTURBATION OF THE DUSHMAN REACTION WITH PIROXICAM: EXPERIMENTAL AND MODEL CALCULATIONS

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Abstract

A novel method for the determination of piroxicam (PX) is proposed and validated. For this purpose, the Bray-Liebhafsky (BL) non-oscillating subsystem (mixture KIO_3 and H_2SO_4), i.e. Dushman reaction (DR) was used. The proposed method relies on the linear relationship between maximal potential shift, ΔE_m, and the logarithm of the injected PX amounts in the concentration range 2.0×10^{-5} mol L^{-1} – 2.0×10^{-4} mol L^{-1}. The sensitivity of the proposed method is 1.5×10^{-5} mol L^{-1}. Some aspects of the possible mechanism of UA action on the DR matrix system are discussed.

Introduction

For developing of kinetic methods for quantitative determination of various analytes [1], besides BL oscillating system, the BL non-oscillating subsystem, i.e. the reaction of reduction of iodate by iodide in acid solution, known as the Dushman reaction (DR) was used [2]. The DR is a part of the highly sensitive BL oscillating system, but it is also a potential medium for analytical procedures.

Different analytical methods for determination of PX were summarized in [3]. Some of those methods are cumbersome, time-consuming or not enough sensitive. Therefore, some new methods based on relatively simple and inexpensive equipment are desirable. Regarding that, the kinetic method based on employing the analyte pulse perturbation technique to the mentioned non-oscillating DR as well as using the potentiometric monitoring of analyte perturbation, promise alternative to some instrumental methods due to its low cost instrumentation and relatively rapid detection procedure.

Experimental

The instrumental equipment included the 52-mL glass CSTR vessel, thermostat, a magnetic stirrer, a potential measuring system and peristaltic pumps. A PC-multilab EH4 16-bit analog-to-digital converter electrochemistry analyzer was directly connected to the reactor through a Pt working electrode and a double junction Ag/AgCl electrode. The procedure is based upon experiments carried out

in acidic iodate solutions and when the inflow concentration of H_2O_2 is zero. Thermostated at 55.0 °C and shielded from light, the reaction vessel was filled up by three separate inflows of 5.9×10^{-2} mol L^{-1} KIO_3, 7.6×10^{-2} mol L^{-1} H_2SO_4 and water, at a maximum flow rate of 5 mL min^{-1}. Then, the inflows were stopped, the stirrer was turned on 900 rpm, and the excess of the reaction mixture was sucked out through the U-shaped glass tube to achieve the actual reaction mixture volume, 22.2 mL. After about 30 min, the inflows were turned on at the required specific flow rate 2.95×10^{-2} min^{-1}, and attained steady state perturbed with different concentrations of PX.

The simulated results were performed using the MATLAB program package. The differential equations derived from the model were integrated using the ode15s solver. All numerical simulations were performed with numerical precision of 10^{-16}.

Results and Discussion

Under the CSTR conditions, the effect of concentration of PX was studied; it is found that a variation of its concentration resulted in a variation in ΔE_m ($\Delta E_m = E_p - E_s$, where E_p is the maximal potential value attained after the performed perturbation and E_s is the potential corresponding to a steady state before the performed perturbation (Fig. 1.)). In the PX concentration range between 2.0×10^{-5} mol dm^{-3} and 2.0×10^{-4} mol L^{-1}, the regression equation of the calibration curve is $\Delta E_m = -214.9 - 43.7 \log (c_{PX}/\text{mol } L^{-1})$ ($r = 0.997$). The detection limit of the method is 1.5×10^{-5} mol L^{-1}.

In order to propose the nature of the interaction of PX with DR matrix, we have used the proposed DR kinetic scheme [4] and suggest that, the PX oxidation, similarly to its interaction with HOBr [5], performs through interaction with HOI, as a crucial step. Figure 1(b) shows the numerically simulated temporal traces upon PX injections in case when model of DR extended with reaction (1) ($k_1 = 6.0 \times 10^4$ mol^{-1} L min^{-1}):

$$PX + HIO \rightarrow PXOH^+ + I^- \qquad (1)$$

The numerically simulated forms of signal profiles obtained before and after perturbation of the DR matrix by the PX are in excellent agreement with experimentally obtained results; the obtained linear concentration range is $3.0 \times 10^{-5} - 2.0 \times 10^{-4}$ mol L^{-1} and regression equation $\Delta E_m = -235.5 - 50.8 \log (c_{PX}/\text{mol } L^{-1})$ ($r = 0.991$).

Conclusion

Our results demonstrate the feasibility of the proposed kinetic method for quantitative determination of PX based on perturbing the Dushman reaction in a steady state. An excellent qualitative and quantitative agreement between the experimental and simulated results indicates that the proposed model mechanism,

though extremely simplified, reflects well the dynamics of PX interaction with the DR, and can be used as a very good starting point for further optimization of the method.

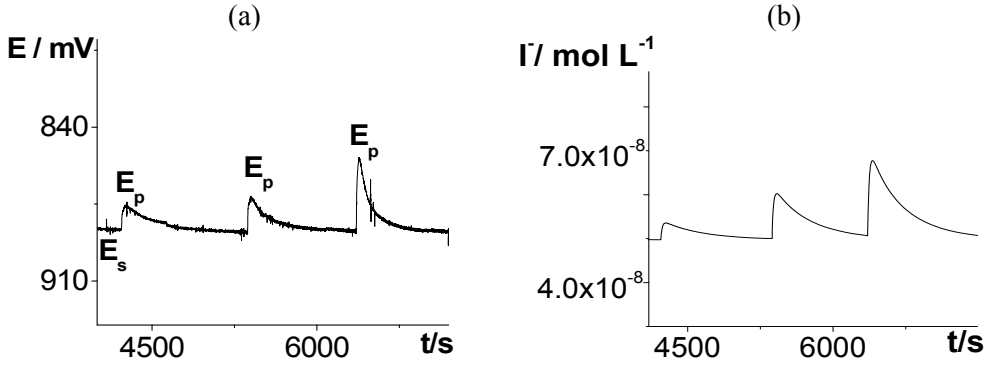

Figure 1. The responses of the DR matrix obtained experimentally (a) and by numerical simulations (b) after its perturbations with different concentrations of PX (from left to right): 1.0×10^{-5} mol L^{-1}, 3.0×10^{-5} mol L^{-1} and 5.0×10^{-5} mol L^{-1}.

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